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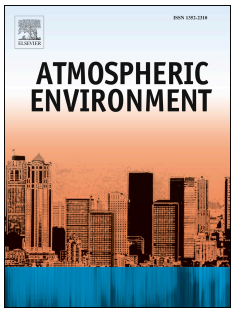

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Concentrations of selected volatile organic compounds at kerbside and background sites in central London

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Abstract

Ground-level concentrations of nine volatile organic compounds (VOCs) were measured using a proton transfer reaction-mass spectrometer (PTR-MS) in central London at an urban background (North Kensington, NK, during 16th - 25th Jan 2012) and a kerbside site (Marylebone Rd, MRd, during 25th Jan - 7th Feb 2012) as part of the winter intensive observation period of the ClearfLo project. Site comparisons indicated that VOC concentrations at the urban background site were significantly lower than at the kerbside site (ratio MRd/NK of 2.3). At the kerbside site PTR-MS measurements of aromatics (benzene, toluene, C_2- and C_3-benzenes) were compared with the gas chromatography – flame ionization detector data from the UK Government's Automatic Hydrocarbon Network. Very good qualitative agreement was observed between the two methods ($r = 0.90 - 0.91$, $p<0.001$, $N = 260$), although there was a significant offset between the instruments. This was partly due to issues with humidity dependent background measurements, but possibly also from isobaric interference of other compounds and their fragments, giving a positive bias to the PTR-MS data. Most compounds showed strong indications of traffic-related sources with double rush hour peaks in diurnal profiles and high correlations with known traffic-related compounds ($r = 0.68 - 0.97$ at NK , 0. 48 - 0.87 at MRd, $p <0.001$, $N_{NK} = 2202-2227$, $N_{MRd} = 2705-2720$) and CO ($r = 0.80-0.96$ at NK, 0.65-0.84 at MRd, p

<0.001, N_{NK} = 223, N_{MRd} = 256-274). Polar plots agreed with statistical analysis of wind direction dependency and identification of potential emission sources was attempted.

1 Introduction

Anthropogenic sources of volatile organic compounds (VOCs) are of particular importance in urban areas due to the intensity of fossil fuel combustion and the relative paucity of biogenic sources in cities. A wide range of VOCs are emitted directly by the evaporation of fuels and solvents, as unburnt fuel and as partially oxidized compounds from combustion processes, mostly vehicle emissions (Kansal, 2009). Some VOCs can directly affect human health (e.g. benzene, which is a known carcinogen) while others contribute to the formation of ozone and aerosol particles in the atmosphere (Derwent, 1995). Both have detrimental effects on human health and the environment (Kim et al., 2001). In winter elevated VOC concentrations are observed due to the shallow daytime boundary layer with limited dilution and mixing. In the UK, VOC emissions are subject to control under European Commission Directive 2008/50/EC. Monitoring networks such as the Automatic Hydrocarbon Network (AHN) provide a running annual mean concentration for a suite of pollutants. Emissions are estimated as part of the National Atmospheric Emission Inventory (NAEI) activity (Yardley et al., 2012).

A wide range of studies focus on VOC concentrations and air quality in cities around the world using diverse measuring techniques (Baker et al., 2008; Jobson et al., 2010). Due to the variety of emission sources, meteorological conditions, and often short atmospheric lifetimes of the compounds, VOC volume mixing ratios can be associated with large variability. Slow response instruments have identified seasonal and diurnal patterns of urban VOC concentrations (Kim et al., 2001), however only fast response instruments have been shown to record this short term variability.

The aim of this study was to:

I. Quantify a suite of VOCs at an urban background and a kerbside site in winter and;
II. Compare VOC volume mixing ratios from fast response PTR-MS measurements with the GC-FID measurements from the Automatic Hydrocarbon Network.

This study was part of the winter intensive observation period of the Clean Air for London project (ClearfLo, www.clearflo.ac.uk), aimed to research boundary layer pollution over London in 2011-2012 (Bohnenstengel et al., in review). Here we report measurements of nine VOC species measured at high temporal resolution at a kerbside and a background site in central London (16th January - 7th February 2012).

2 Methods

2.1 Measurement sites and meteorology

Details of both the North Kensington (NK) background and Marylebone Rd (MRd) kerbside sites are compared (Supplementary content Table A1). Air was pumped through a PTFE inlet (and PTFE filter at MRd) attached to 1/4" OD PTFE tubing to a high sensitivity proton transfer reaction-mass spectrometer (PTR-MS; Ionicon Analytik GmbH, Innsbruck, Austria).

Meteorological measurements were co-located with the inlet at NK (Figure 1 and Supplementary content Table A1). The mean UK temperature in January was 6.0 °C, i.e. 1.3 °C above the 1971-2000 average (UK Met Office, 2012), although February experienced low temperatures and snowfall, which is uncommon in London.

2.2 VOC sampling

VOC mixing ratios were measured on-line using a PTR-MS (de Gouw and Warneke, 2007; Lindinger et al., 1998). The instrument was operated in multiple ion detection (MID) and mass scan (SCAN) modes (Supplementary content A1). In MID mode the quadrupole mass spectrometer scanned through 11 pre-determined masses, to which the following compounds were ascribed: *m/z* 21 (indirect quantification of *m/z* 19 primary ion count [H_3O^+] via isotopologue [$H_3{}^{18}O^+$]), *m/z* 33 (methanol), *m/z* 39 (indirectly quantified *m/z* 37 first cluster [$H_3O^+.H_2O^+$]), *m/z* 42 (acetonitrile), *m/z* 45 (acetaldehyde) *m/z* 59 (acetone/propanal), *m/z* 69 (cycloalkanes/isoprene), *m/z* 79 (benzene), *m/z* 93 (toluene), *m/z* 107 (C_2-benzenes) and *m/z* 121 (C_3-benzenes).

The UK national Automatic Hydrocarbon Network (AHN) station at MRd measures 29 different hydrocarbons using a gas chromatography-flame ionization detector (GC-FID, AutoSystem XL; PerkinElmer Inc., USA). This method complies with standards set out by the European Air Quality Directive (Broadway and Tipler, 2008). A 40 min continuous sampling period provides hourly means (Supplementary content A2).

PTR-MS measures in unit mass resolution and a fragment may derive from several parent compounds, therefore each detected mass may relate to one or more compounds. Where possible, measurements should be verified by more specific analytical techniques, such as GC-FID. Unfortunately, only benzene, toluene, some C_2- and C_3-benzenes were verified by the AHN.

2.3 Quality analyses and data handling

The PTR-MS was calibrated over a range of concentrations using a certified multi-component VOC gas standard (Ionimed Analytik GmbH, Austria). The measured instrument sensitivities were then used to convert normalized count rates of RH^+ to volume mixing ratios (Langford et al., 2010a). The

instrument background was quantified using a platinum catalyst and subtracted from the ambient measurements. Since the background was determined for dry air, corrections for humidity effects on some compounds had to be applied and were associated with large uncertainties (Supplementary content B).

A low pass filter was applied to smooth the data and reduce instrumental noise. Spearman's rank correlation coefficients and Wilcoxon rank sum tests were used in statistical analyses due to the data distributions.

3 Results & Discussion

3.1 VOC concentrations

VOC concentrations measured by the PTR-MS at the North Kensington (NK) background site (Figure 2a) and at the Marylebone Rd (MRd) kerbside site (Figure 2b) are summarized in Table 1a and 1b. At both sites methanol, acetaldehyde and acetone, all oxygenated compounds, were the most abundant. Methanol has a variety of biogenic, anthropogenic and atmospheric sources (Cady-Pereira et al., 2012). Acetone has some biogenic contributions but solvents and tailpipe emissions were most likely the main sources (de Gouw et al., 2005; Reissell et al., 1999; Warneke et al., 1999). Both have a low photochemical reactivity with OH resulting in longer atmospheric lifetimes, which also contributed to the relatively high mixing ratios. The compounds with the lowest mixing ratios at both sites were acetonitrile and cycloalkanes/isoprene. Although these are emitted from vehicle exhaust, their volume mixing ratios were much lower than other traffic-related compounds. The isoprene component of *m/z* 69 was estimated at 22% and presumably from traffic as the biogenic component was absent due to the season (Borbon et al., 2001). Comparison with GC-FID isoprene concentrations at NK inferred that cycloalkanes provided a significant contribution to *m/z* 69 (Supplementary content C) (Erickson et al., 2014 ;Yuan et al, 2014). Although globally biomass burning is the main source of acetonitrile (Holzinger et al., 2001), in urban areas emissions from vehicle exhaust are prominent as diurnal profiles resembled a double rush hour pattern (Section 3.4) with some increased acetonitrile emissions occurring at low temperatures possibly from solid fuel burning (Section 3.3).

Mixing ratios for most of the compounds agreed with or were lower than observations from other urban areas, but benzene and C_2-benzenes concentrations were slightly higher at MRd compared with previous observations in UK cities (Langford et al., 2009, 2010b). The measurement proximity to the source emissions must be considered; for example, Langford et al. (2010b) reported concentration measurements from tall towers where the effects of dilution and photochemical loss are greater.

During both measurement periods the beginnings and ends were marked by high pollution episodes (16^{th} -18^{th}, 24^{th} -28^{th} Jan and 3^{rd} -7^{th} Feb).

3.1.1 Site comparison

The volume mixing ratios of all compounds were significantly different ($p < 0.001$) between NK and MRd, except for acetone ($p = 0.26$). Acetone has a relatively long atmospheric lifetime (Table 1a) and therefore mixing ratios are often homogenous over larger areas. Apart from methanol, which was 1.5 times higher at NK, the remaining compounds were up to 3 times higher at the MRd site with a mean site ratio (MRd/NK) of 2.3. This difference is related to the proximity to sources and differences of source strengths. Comparison of both time periods using the AHN data from MRd showed that aromatic compounds were significantly higher ($p<0.001$) during the first period indicating that the differences between the sites were indeed due to the location. These compounds are found in tailpipe emissions, which so close to a heavily trafficked road was the main source. In general, NK represents an urban location away from major sources and broadly representative of city-wide background concentrations, e.g. urban residential areas, whereas MRd, an urban kerbside site next to a major arterial route, represents central urban areas such as surrounding the congestion charge zone in London.

3.2 Comparisons with the Automatic Hydrocarbon Network and PTR-MS quantification limitations

Benzene, toluene, C_2- and C_3-benzenes from PTR-MS measurements were compared with the same compounds or sum of compounds with similar masses measured by GC-FID in the framework of the Automatic Hydrocarbon Network (AHN). Due to isobaric interference within the PTR-MS measurements the sum of available GC-FID measurements was used for compounds with a protonated mass of *m/z* 107 and *m/z* 121. Direct comparisons of 1h mean (±2.9-5.9% SE) PTR-MS and GC-FID measurements (Figure 3) are summarized in Table 2. The PTR-MS data for these compounds corresponded to within a factor of 1.3 for *m/z* 79, 93 and 107, and a factor of 2.5 for *m/z* 121 ($p<0.001$). Comparison of the time series showed that the PTR-MS measurements closely followed the diurnal variations of the GC-FID measurements (Figure 3).

As the PTR-MS cannot distinguish between compounds with similar masses, isobaric interference can occur, e.g. benzaldehyde can produce mass interferences for C_2-benzenes (Warneke et al., 2003). The *m/z* 107 likely has four contributing species: ethyl benzene, (m+p)-xylene, o-xylene, and some benzaldehyde. C_3- benzenes may include a wider range of compounds: propyl benzene, two ethyl methyl benzenes and three trimethylbenzene isomers. The AHN measurements included all of the above for m/z 107, but only three trimethylbenzene isomers at *m/z* 121.

Humidity dependencies on instrument sensitivities and background were thoroughly investigated in the laboratory after the campaign. Calibrations showed no significant variations of sensitivity with humidity. Corrections were applied to compounds showing humidity effects on instrument background, but not all effects could be recreated and accounted for, such as humidity effects on inlet impurities affecting aromatics (Supplementary content B).

Fragmentation can become a concern at higher *E/N* ratios (de Gouw and Warneke, 2007; Maleknia et al., 2007; Warneke et al., 2003). An *E/N* ratio of 125 Td was used in this study as this represents a compromise between reagent ion clustering and fragmentation suppression (Hewitt et al., 2003). Some fragmentation can still occur, as several studies using a coupled GC-PTR-MS with a range of *E/N* ratios have identified various fragment ions. Benzaldehyde, ethyl benzene and xylene isomers with *m/z* 107 may produce fragments of about 30-40% at *m/z* 79 with higher *E/N* ratios (Maleknia et al., 2007), as well as propyl benzene isomers and smaller contributions of fragments of butyl benzene (Warneke et al., 2003). As only o-xylene was present in the calibration standard, fragments from other compounds at that mass cannot be accounted for and are likely to have contributed to the increased PTR-MS signal. It is estimated that with an electrical field strength of 125 Td around 15% C_2-benzenes may have contributed to *m/z* 79. Interference from fragments at *m/z* 93 could include a range of biogenic terpenes and their isomers (Maleknia et al., 2007).

Previous studies have shown that there is good correlation between PTR-MS and GC-FID, however the quantitative agreement can be poor with differences of up to a factor of 2 (de Gouw and Warneke, 2007; Kato et al., 2004). The value for *m/z* 121 is somewhat higher than cited in the literature, which may be due to humidity effects on inlet impurities which could not be accounted for after the campaign, as well as isobaric interference from compounds and fragments not measured by the AHN. All four *m/z* showed very good correlations (Figure 4) with r 0.90-0.91 ($p<0.001$) in agreement with literature values (Kuster et al., 2004; Langford et al., 2010b).

3.2.1 Correlations with carbon monoxide

Carbon monoxide (CO) concentrations were used for correlations and ratios with VOCs to determine whether the VOC sources were from fuel combustion (Table 3), as CO is a suitable marker for anthropogenic combustion emissions.

High correlations for acetonitrile against CO indicate that fuel burning was likely the primary source at NK. Correlations with CO were higher for PTR-MS than GC-FID (r 0.65 – 0.75, $p<0.001$ for PTR-MS; r 0.58-0.68, $p<0.001$ for GC-FID). Possibly the higher temporal resolutions and the longer sampling time of the PTR-MS allowed the detection of short-term variations in emission patterns.

3.3 VOC correlations and ratios

Correlations between the different VOCs yielded coefficients (r) ranging between -0.23 and 0.97 at NK and -0.20 to 0.87 at MRd ($p<0.001$). The poorer correlations involved methanol (r -0.23 - 0.35). Methanol has a variety of different sources, which in this case had little commonality with the other compounds. Strong linear correlations (r 0.67 - 0.97 at NK, 0.48 - 0.87 at MRd) indicate that the other compounds shared some or almost all sources, however, bimodal distributions can relate to multiple separate sources. In winter, vehicle exhaust and, to a small extent, evaporative emissions account for a majority of the sources. The r-values at MRd were lower than at NK showing more scatter (Figure 5). This may reflect a sequential sampling artefact due to the instrument continuously cycling through the different *m/z*, combined with highly variable concentrations at this site. Alternatively, it may represent true variability in the nearby emission source; within traffic emissions, diverse types of vehicles, fuels, and driving patterns result in different traffic related VOC ratios (Figure 5, A and B), which can be detected by online methods as the compounds reach the inlet with little mixing (Chan et al., 1991; Chan et al., 2002).

Biomass burning for heating may explain a secondary source contribution to acetonitrile at MRd, as it mostly occurs with cold temperatures and is not shared with benzene, hence is not related to traffic emissions (Figure 5 D).

Using temperature as a third variable can illustrate temperature dependencies of source contributions. Cycloalkanes/isoprene and benzene show a good correlation (r = 0.77 and 0.80) as they are present in tailpipe emissions (Park et al., 2011) with a seasonally low biogenic component (Figure 5, E and F). The main source of most C_2- and C_3-benzenes are motor vehicle emissions (Heeb et al., 2000) which was reflected in the high correlations (0.72 to 0.97, $p<0.001$). These aromatics have a shorter atmospheric lifetime making them important factors in urban photochemical smog production (Table 1a).

Benzene-to-toluene (b/t) ratios can indicate the photochemical age of the pollution carried by air masses (Warneke et al., 2001 and references therein). Due to seasonally low OH concentrations, only changes in b/t ratios over longer periods were considered to be representative of air mass transport.

The median (IQR) b/t ratios were around 0.6 (0.43-0.80) at both sites and agreed with previous values (Chan et al., 2002; Heeb et al., 2000; Langford et al., 2009), as well as with those from the AHN at MRd with a median of 0.6 (0.48-0.76) ($r=0.90$, $p<0.001$). These b/t ratios are consistent with the air mass footprints derived from the UK Met Office's Numerical Atmospheric-dispersion Modelling Environment (NAME) (Jones et al., 2007) using Unified Model (UM) Met data (Figure 6).

This model simulates the origin of the air masses affecting the ClearfLo sites within the previous 24h (Bohnenstengel et al., in review). Shifts between high and low pollution episodes often are correlated with changes in wind direction and intensity. For the low pollution periods (19th-23rd Jan and 31st Jan-2nd Feb) strong westerlies brought air masses with regional influences and high b/t ratios of 0.91 (0.64-1.31). The high pollution episodes (24th -25th Jan and 4th Feb) showed low wind speeds resulting in shorter travel distances of the air masses and stronger local London influences (up to 87%, campaign average 37%) and corresponding low b/t ratios of 0.48 (0.39-0.58).

3.4 Diurnal averages

Meteorological conditions can mask emission patterns, therefore diurnal averages are used to aid in their identification (Figure 7). Concentrations can depend on the mixing height in the boundary layer, however LIDAR measurements showed little diurnal variation in the seasonally shallow mixing height (500-1000m) (Bohnenstengel et al., in review). All compounds, bar methanol, showed a double rush hour peak during weekdays (07:00-10:00 and 17:00-20:00 GMT) and lower concentrations with less variability on weekends (Figure 7, E - H), suggesting vehicle exhaust as a major source. At MRd, rush hour peaks were less pronounced due to the continuously high daytime traffic density (68002 vehicles per day; Department for Transport, 2012), which causes the road to saturate for prolonged periods during the day.

The early morning minima (04:00 – 06:00 GMT) can be attributed to reduced human activity which sharply increases during the morning rush hour peak (07:00-10:00 GMT) (Figure 7, F – H). Methanol and acetone have numerous sources and longer atmospheric lifetimes resulting in no clear diurnal pattern (Figure 7, A and B).

3.5 Analyses of wind direction dependence

3.5.1 Synoptic polar plots

Using wind speed and direction measurements from the BT tower (190 m a.g.l.), polar plots were constructed for compound mixing ratios (Figure 8) using a generalized additive model (GAM) (Hastie and Tibshirani, 1990; Wood, 2006) to interpolate between averaged data points in the R package openair (Carslaw, 2012; Carslaw and Ropkins, 2012). At NK high concentrations for most compounds were associated with low wind speeds (i.e. <5 m s^{-1}) indicating local emission sources. Methanol showed high concentrations with WSW wind directions and speeds >5 m s^{-1} possibly representing pollution transported to the site from a biodiesel production facility located 1km SW of the site. Biodiesel production from waste cooking oil by transesterification often involves evaporating methanol.

At MRd methanol showed high concentrations with S and N winds >10 m s^{-1}, whereas benzene is representative of the other compounds with patches of increased concentrations at speeds of 5-10 m s^{-1}. The WSW and ENE patches coincide with the directional layout of Marylebone Rd, while the SSW source may originate from traffic in the Marble Arch/Hyde Park Corner area, which boasted the highest annual mean traffic count of 100574 motor vehicles per day in all of Westminster, London (DfT, 2012).

3.5.2 Synoptic wind direction dependencies and comparison with NAEI

To quantify wind direction dependencies (Section 3.5.1) and compare measured VOC mixing ratios at MRd with the National Atmospheric Emissions Inventory (NAEI) for estimated emissions, general linear models were used for each compound concentration against the four wind direction categories. There was no significant difference in wind speed with direction. Correlations of VOC concentrations with wind speed showed weak negative relationships ($r = -0.38$ to -0.14, $p < 0.05$) indicating that a dilution effect depending on wind speed from above-canyon air mass mixing may play a small role in street canyon concentrations.

All species showed significant differences in mixing ratios with wind direction (F- statistic 6.73 - 41.8, $p < 0.001$ for measured compounds; $F = 4.48$, $p<0.01$ for estimated benzene) and agreed with the polar plots. Differential source density within the four sectors and fetch variability over the city are likely reasons.

Estimated emissions and observed concentrations for benzene agreed that low emission source densities to the N resulted in low observed mixing ratios. The largest estimated emissions were to the E, whereas measurements indicated the S. Regent's Park to the N and Hyde Park to the S have large areas of low emissions reducing the estimates in these sectors. Emission estimates also ignore background values from greater fetch across London. High localized emission sources seen in the polar plots (Figure 8) could be responsible for higher measured VOC concentrations to the W and S, which partially agrees with the high estimated emissions from the nearest westerly grid cell. Estimated emissions from the NAEI are integrated over 1 km^2 grid resolution, but localized sub-grid scale effects may be masked by the grid averaging area. It must be emphasized that the volume mixing ratios were measured at ground-level within the street canyon, whereas the wind data are representative of synoptic winds above the street canyons.

4 Conclusion

High VOC concentrations during the winter in urban locations are mostly from traffic emissions. This was reflected at both sites in diurnal profiles, VOC/VOC and VOC/CO correlations and ratios, wind sector dependence analyses and polar plots. Measurements at the NK background site indicated

significantly lower mixing ratios than at the MRd kerbside site, even though AHN data showed that kerbside concentrations were higher during the first measurement period, suggesting site differences due to the location with different source strengths and proximity.

Comparison of PTR-MS and GC-FID data from MRd for aromatics showed good correlation and qualitative agreement. However, PTR-MS data were significantly higher possibly due to some isobaric interference from additional compounds and fragments, and possibly systematic errors introduced during instrument background corrections. Short term variations in the ratio of traffic related compounds from differences in traffic density, driving style, vehicle and fuel types were observed by PTR-MS at MRd site and higher correlations with CO for PTR-MS than the GC-FID measurements were likely due to the fast response and longer sampling times of the PTR-MS. The AHN can only report hourly arithmetic means due to the methods employed, possibly leading to a reporting bias and a loss of information on short term variability.

Elevated concentrations were mostly observed when synoptic-scale wind speeds were low at NK as dispersion of localised emissions was reduced. However, some non-local emission sources were detected using polar plots and possible sources were identified. There were significant differences in VOC concentrations with wind direction. When compared with estimated benzene emissions by the NAEI, estimates were less representative when VOC concentrations were high, as they are unable to capture the influence of city background emissions and reduced local sub-grid emission source contributions.

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Figure 1. *Top*: 5 min means of ambient air temperature (°C) and relative humidity (%) during the campaign 16th Jan – 7th Feb 2012. *Bottom*: Frequency plots of mesoscale wind direction (%) with subcategories of wind speed (m s^{-1}) using 30 min mean data from the WXT520 (Vaisala Ltd) at 190m on the BT tower at NK (16th – 25th Jan 2012) (*left*) and MRd (25th Jan – 7th Feb 2012) (*right*).

Figure 2. 5min mean (grey) and 25 min means (black) with detection limits (dashed line) for all measured VOCs (ppb) at **(a)** North Kensington and **(b)** Marylebone Rd (16th Jan – 7th Feb 2012). *M/z* are 33 (methanol), 42 (acetonitrile), 45 (acetaldehyde), 59 (acetone), 69 (cycloalkanes/isoprene), 79 (benzene), 93 (toluene), 107 (C_2-benzenes) and 121 (C_3-benzenes).

Figure 3. 1h means for benzene, toluene, C_2- and C_3-benzenes mixing ratios (ppb) measured by the PTR-MS (solid line) and GC-FID (dashed line) at Marylebone Road (25th Jan – 7th Feb 2012).

Figure 4. Scatter plots of 1h mean VOC concentrations (ppb) (benzene, toluene, C_2- and C_3-benzenes) of PTR-MS against GC-FID measurements at Marylebone Road (25th Jan – 7th Feb 2012) with reduced major axis (RMA) linear regressions, ± 99th confidence intervals, 1:1 line (dotted) with r-values.

Figure 5. Scatter plots of representative VOC correlations measured at North Kensington (left) and Marylebone Rd (right) (16th Jan – 7th Feb 2012) using 5 min means (ppbv) with ambient air temperature (°C) at time of sampling (colour bar).

Figure 6. 24 hour back trajectories from the Met Office NAME dispersion model at North Kensington (16th Jan-7th Feb 2012). Daily release for 3 hours from midday (20 m height) tracking the surface layer only (0-100m) for the 24 hours prior. Reproduced with permission from Zoë Fleming (NCAS, University of Leicester).

Figure 7. Diurnal plots of 25min averages (ppb) for representative VOCs at North Kensington and Marylebone Road (16th Jan – 7th Feb 2012) with the 95% confidence interval (shaded areas), all days (solid line), weekdays (dashed line) and weekends (dotted line).

Figure 8. Representative selection of polar plots of synoptic wind speed (m s^{-1}) against wind direction (°) from the BT tower (190m) with VOC mixing ratios (ppb) as a third variable (colour bar) for methanol (*m/z* 33), acetonitrile (*m/z* 42) and benzene (*m/z* 79) at North Kensington (16th -25th Jan 2012) (*top*) and Marylebone Rd (25th Jan – 7th Feb 2012) (*bottom*).

463

464 **Table 1a. Summary of 5 min averages of VOC mixing ratios (ppb) at North Kensington, London (16th - 25th Jan 2012).**

Mixing ratios **(ppb)**	*Methanol* **m/z 33**	*Aceto-nitrile* **m/z 42**	*Acetal-dehyde* **m/z 45**	*Acetone* **m/z 59**	*Cycloalkanes/ Isoprene* **m/z 69**	*Benzene* **m/z 79**	*Toluene** **m/z 93**	*C_2-benzenes* **m/z 107**	*C_3-benzenes* **m/z 121**
Lifetime (OH^a)	*12 d*	*1.5 yr*	*8.8 h*	*53 d*	*1.4 h*	*9.4 d*	*1.9 d*	*5.9 h[b]*	*4.3 h[c]*
N	2219	2202	2211	2213	2199	2227	2226	2225	2226
LoD	*0.37*	*0.04*	*0.18*	*0.06*	*0.005*	*0.04*	*0.01*	*0.08*	*0.03*
Min.	2.86	*<LoD*	*<LoD*	0.37	*<LoD*	*<LoD*	0.03	*<LoD*	0.04
1st quartile	5.06	0.05	0.29	0.95	0.08	0.14	0.21	0.23	0.24
Median	5.77	0.06	0.46	1.16	0.14	0.24	0.42	0.44	0.37
Geom. mean	6.17	0.07	0.50	1.25	0.13	0.24	0.42	0.45	0.40
Arithm. mean	6.40	0.08	0.62	1.34	0.17	0.31	0.60	0.63	0.50
3rd quartile	8.00	0.07	0.75	1.51	0.21	0.39	0.74	0.79	0.59
Max.	10.4	0.10	3.67	6.79	0.98	2.13	4.92	4.89	3.65
SD	1.84	0.05	0.51	0.67	0.13	0.26	0.61	0.62	0.42
Skew	0.39	2.09	2.08	3.02	1.90	2.19	2.53	2.62	2.61
Kurtosis	-0.89	6.03	5.25	13.5	4.85	6.96	8.71	9.45	9.36

465 [a] Atmospheric lifetimes with regard to OH for a 12-h daytime average OH radical concentration of 2.0 x 10^6
466 molecule cm^{-3} (Atkinson, 2000).
467 [b] example using m-xylene.
468 [c] example using 1,2,4-trimethylbenzene.
469

470 **Table 1b. Summary of 5min averages of VOC mixing ratios (ppb) at Marylebone Rd, London (25th Jan - 7th Feb 2012).**

Mixing ratios **(ppb)**	*Methanol* **m/z 33**	*Aceto-nitrile* **m/z 42**	*Acetal-dehyde* **m/z 45**	*Acetone* **m/z 59**	*Cycloalkanes/ Isoprene* **m/z 69**	*Benzene* **m/z 79**	*Toluene* **m/z 93**	*C_2-benzenes* **m/z 107**	*C_3-benzenes* **m/z 121**
N	2712	2718	2716	2705	2720	2715	2713	2708	2715
LoD	*0.37*	*0.04*	*0.18*	*0.06*	*0.005*	*0.04*	*0.01*	*0.08*	*0.03*
Min.	1.34	0.08	0.38	0.70	0.15	0.06	0.02	*<LoD*	0.05
1st quartile	3.47	0.16	0.92	0.95	0.31	0.38	0.49	0.81	0.50
Median	5.00	0.19	1.34	1.15	0.39	0.56	0.80	1.21	0.86
Geom. mean	4.48	0.19	1.39	1.20	0.41	0.55	0.85	1.21	0.85
Arithm. mean	4.67	0.20	1.61	1.25	0.44	0.63	1.18	1.45	1.11
3rd quartile	5.61	0.24	2.07	1.47	0.53	0.81	1.50	1.87	1.52
Max.	7.39	0.56	6.18	3.78	1.18	3.57	10.0	7.60	4.76
SD	1.27	0.07	0.92	0.38	0.17	0.35	1.13	0.9	0.79
Skew	-0.47	1.33	1.29	1.21	1.05	1.68	2.8	1.62	1.21
Kurtosis	-0.72	2.28	1.53	2.04	0.65	5.36	11.6	0.02	1.20

471
472

473 **Table 2 Summary of 1h averages of compounds (ppb) measured by both PTR-MS and GC-FID at Marylebone Rd, London**
474 **(25th Jan – 7th Feb 2012).**

	PTR-MS				GC-FID			
Mixing ratios	*Benzene*	*Toluene*	*C_2-benzenes*	*C_3-benzenes*	*Benzene*	*Toluene*	*C_2-benzenes*	*C_3-benzenes*
(ppb)	***m/z 79***	***m/z 93***	***m/z 107***	***m/z 121***	***m/z 79***	***m/z 93***	***m/z 107***	***m/z 121***
N	274	274	274	256	302	302	302	302
LoD	*0.04*	*0.01*	*0.08*	*0.03*	*0.01*	*0.01*	*0.01*	*0.01*
Min.	0.17	0.13	0.29	0.13	0.14	0.07	0.03	0.01
1st quartile	0.39	0.52	0.87	0.46	0.30	0.38	0.57	0.13
Median	0.57	0.82	1.23	0.91	0.42	0.61	0.83	0.24
Geom. mean	0.58	0.95	1.30	0.81	0.41	0.66	0.86	0.24
Arithm. mean	0.63	1.17	1.44	1.07	0.47	0.87	1.01	0.33
3rd quartile	0.82	1.53	1.89	1.51	0.58	1.09	1.32	0.46
Max.	2.26	6.42	5.12	3.71	1.42	5.17	4.51	1.45
SD	0.32	1.01	0.81	0.74	0.23	0.83	0.63	0.29
Skew	1.30	2.06	1.38	0.93	1.53	2.33	1.39	1.27
Kurtosis	2.65	5.21	2.53	0.39	2.98	6.36	2.13	1.16

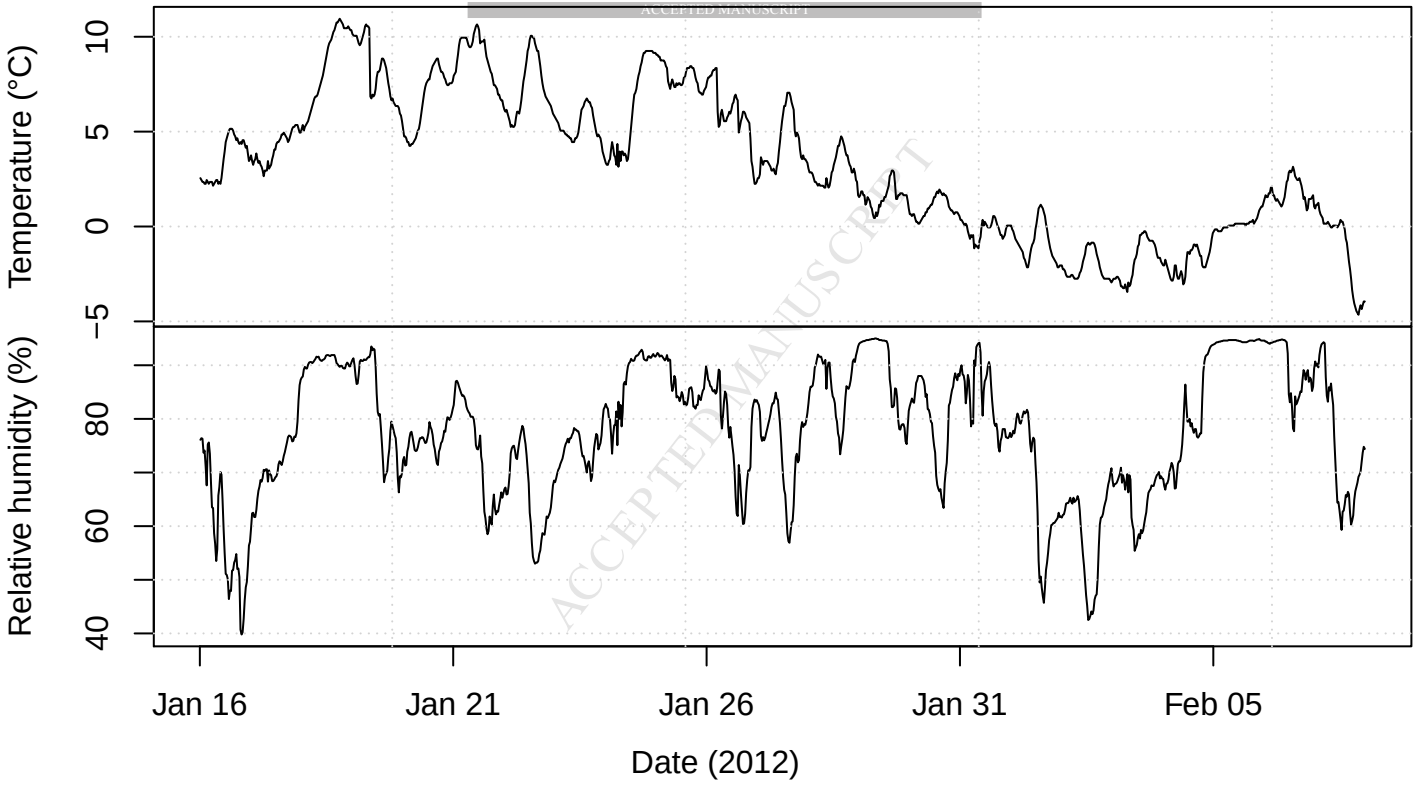
475

476

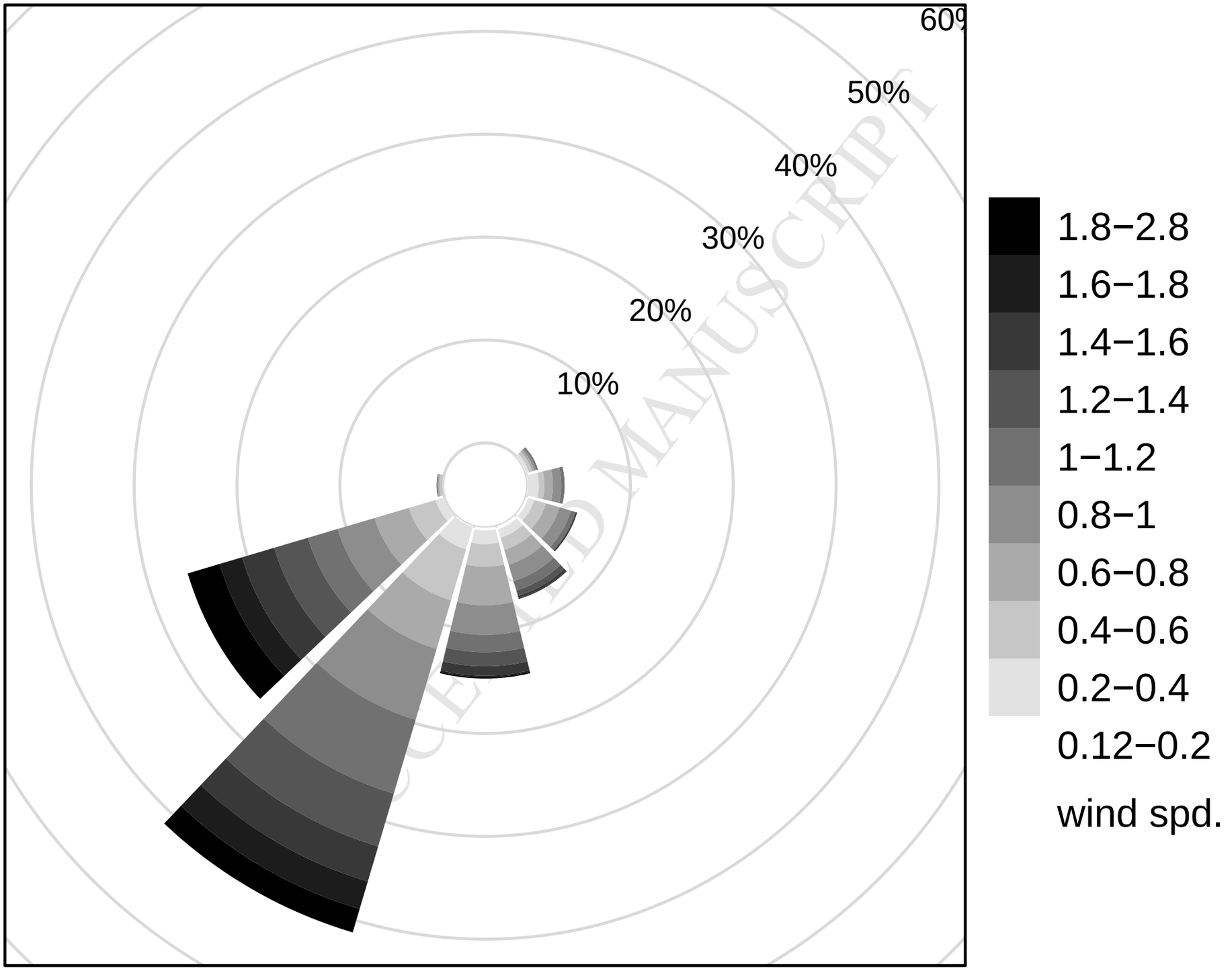
477 **Table 3. Mean VOC/CO ratios for volume mixing ratios (ppbv/ppbv) at NK and MRd, London (16th Jan - 7th Feb 2012).**

Compound	*ClearfLo*					
	NK[a]		***MRd***			
	PTR-MS		*PTR-MS*[b]		*GC-FID*[c]	
	[VOC]/[CO]	*r*	*[VOC]/[CO]*	*r*	*[VOC]/[CO]*	*r*
Methanol	2.13E-02	0.28	1.20E-02	0.27		
Acetonitrile	2.70E-04	0.87	5.21E-04	0.55		
Acetaldehyde	2.14E-03	0.93	4.14E-03	0.84		
Acetone	4.53E-03	0.62	3.18E-03	0.74		
Cycloalkanes/ Isoprene	5.74E-04	0.80	1.13E-03	0.82		
Benzene	1.08E-03	0.96	1.59E-03	0.75	1.58E-03	0.68
Toluene	2.07E-03	0.93	3.09E-03	0.72	3.33E-03	0.65
C2-benzenes	2.16E-03	0.89	3.69E-03	0.66	4.70E-03	0.58
C3-benzenes	1.72E-03	0.86	2.60E-03	0.65	1.61E-03	0.68

478 [a]N = 226, [b]N =256-274, [c]N =302
479

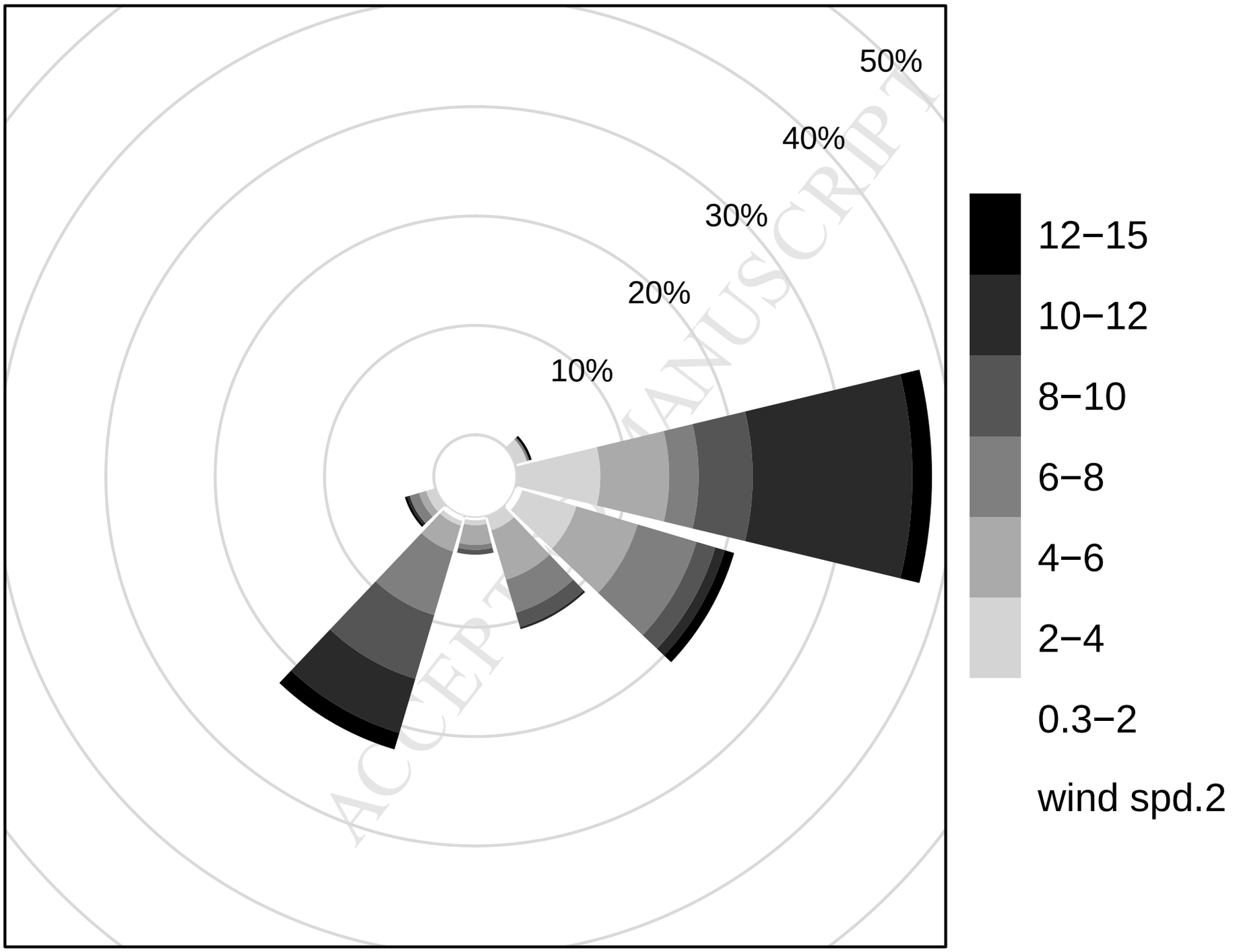


North Kensington wind frequency

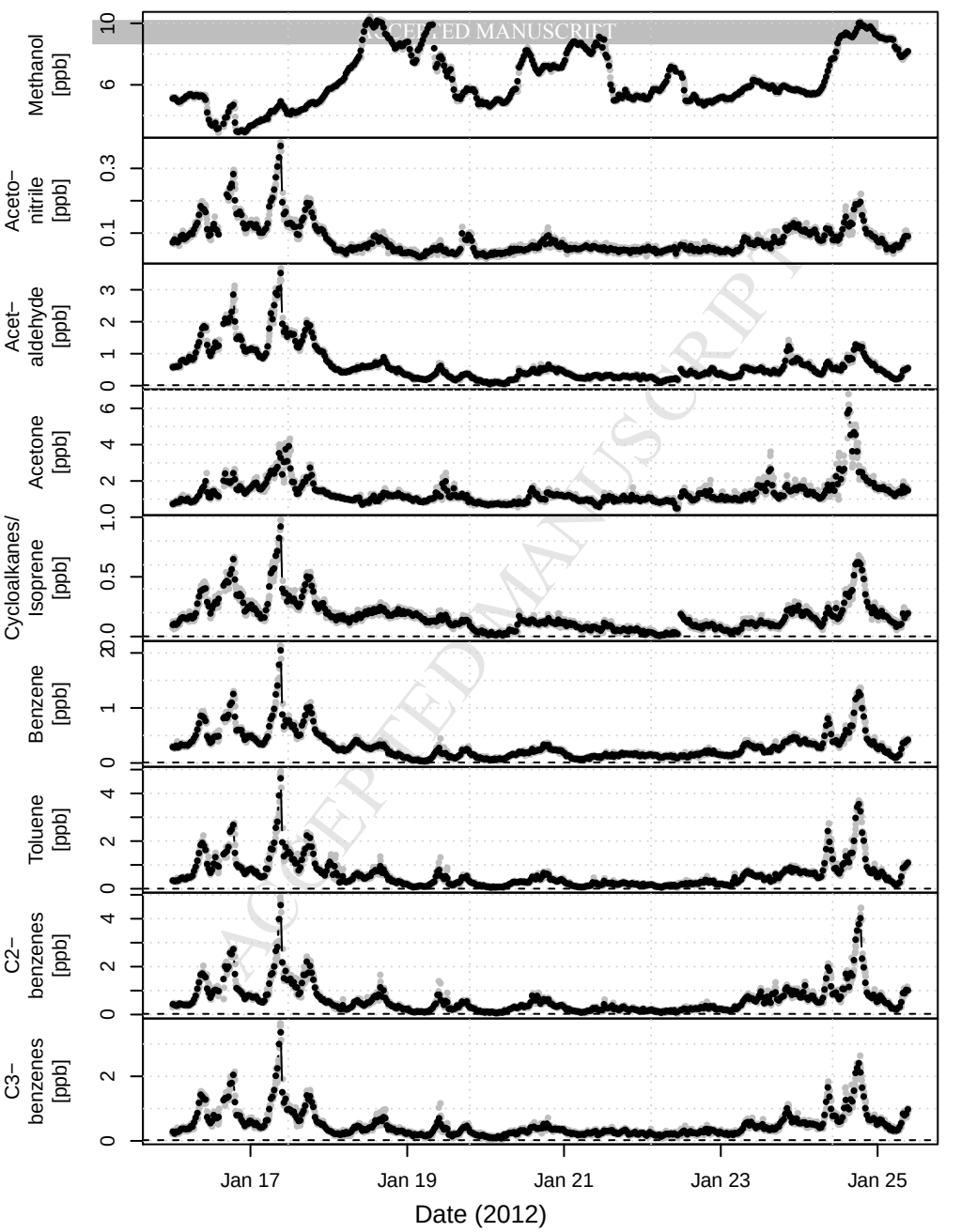


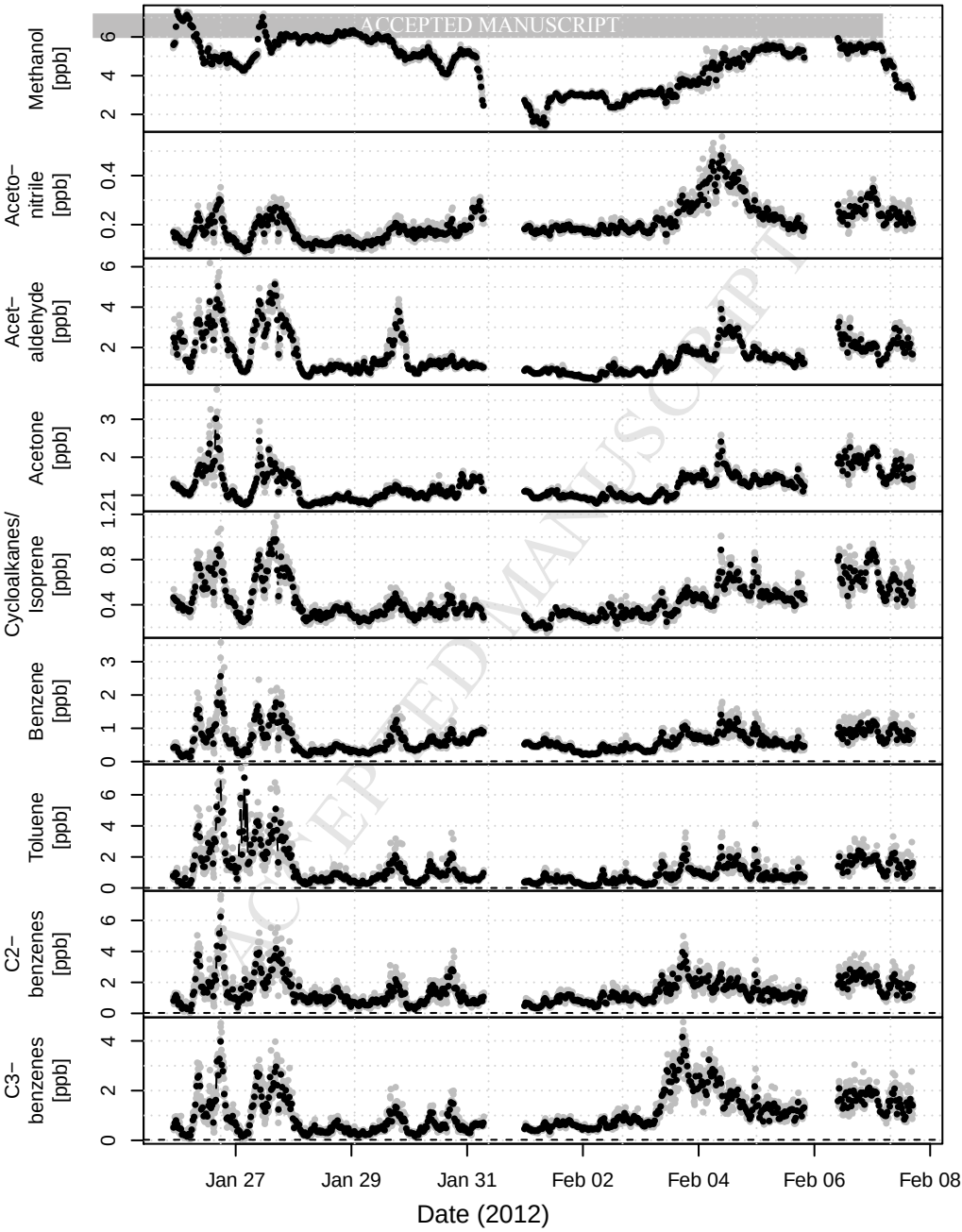
Frequency of counts by wind direction (%)

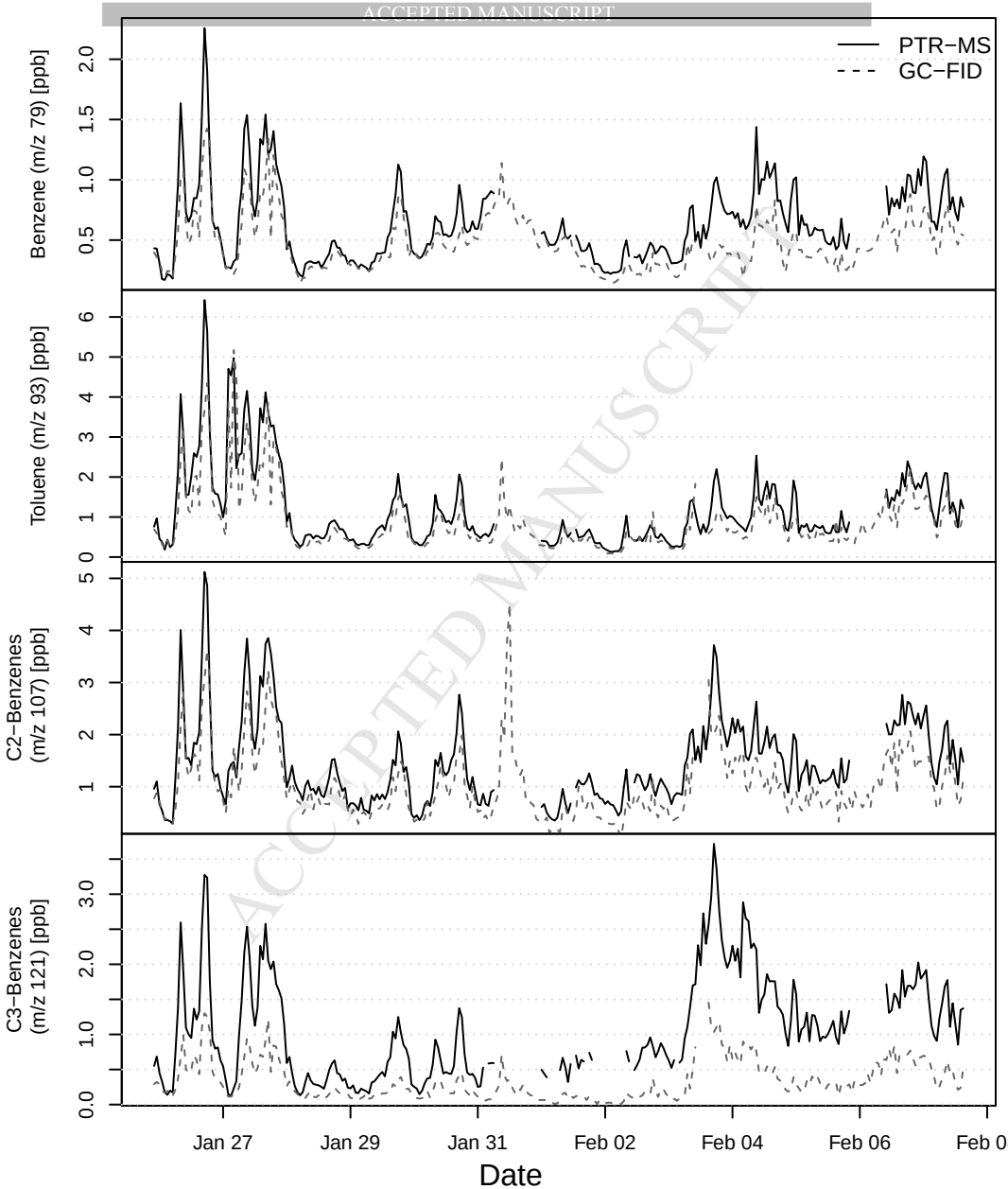
Marylebone Rd wind frequency

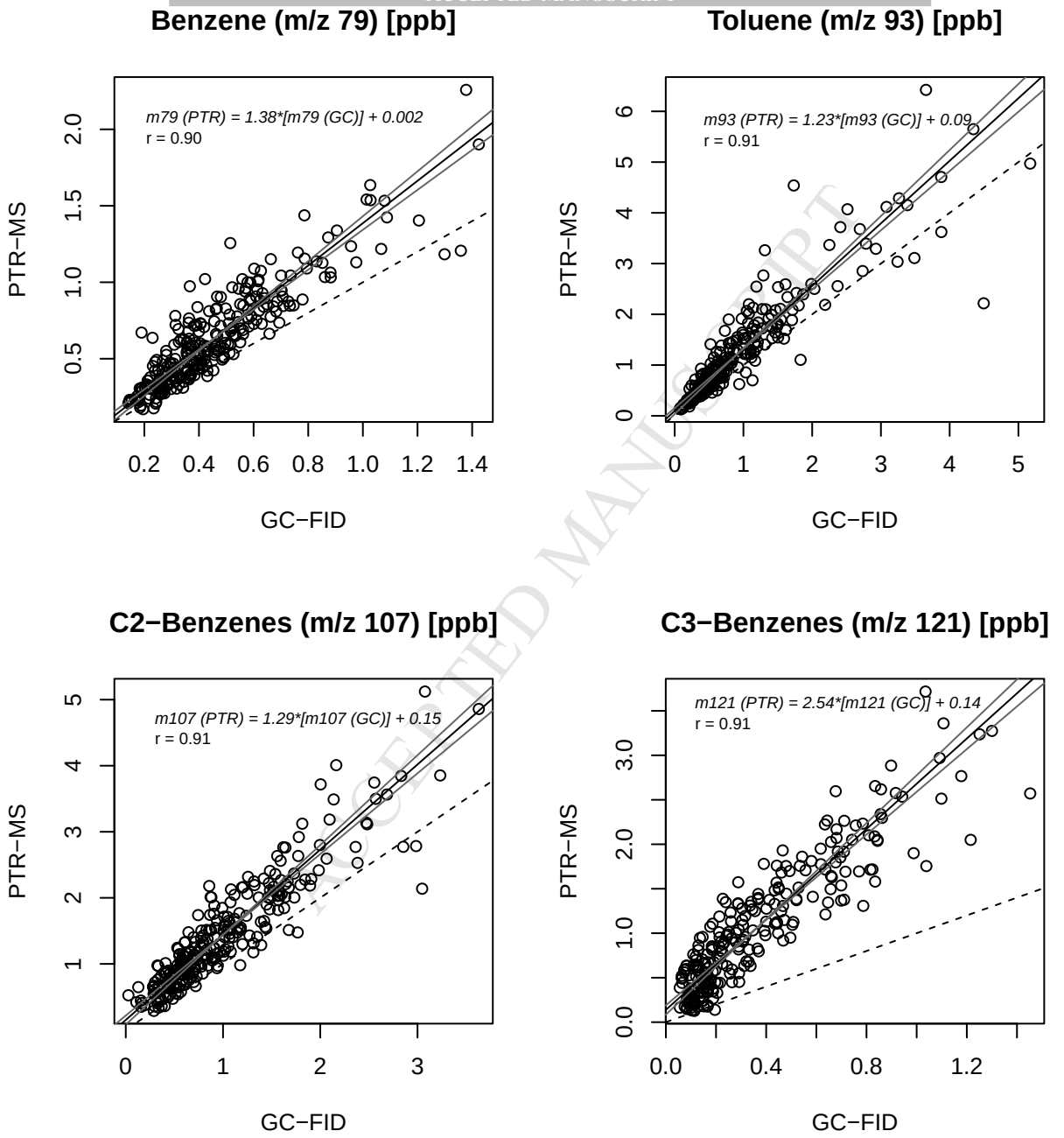


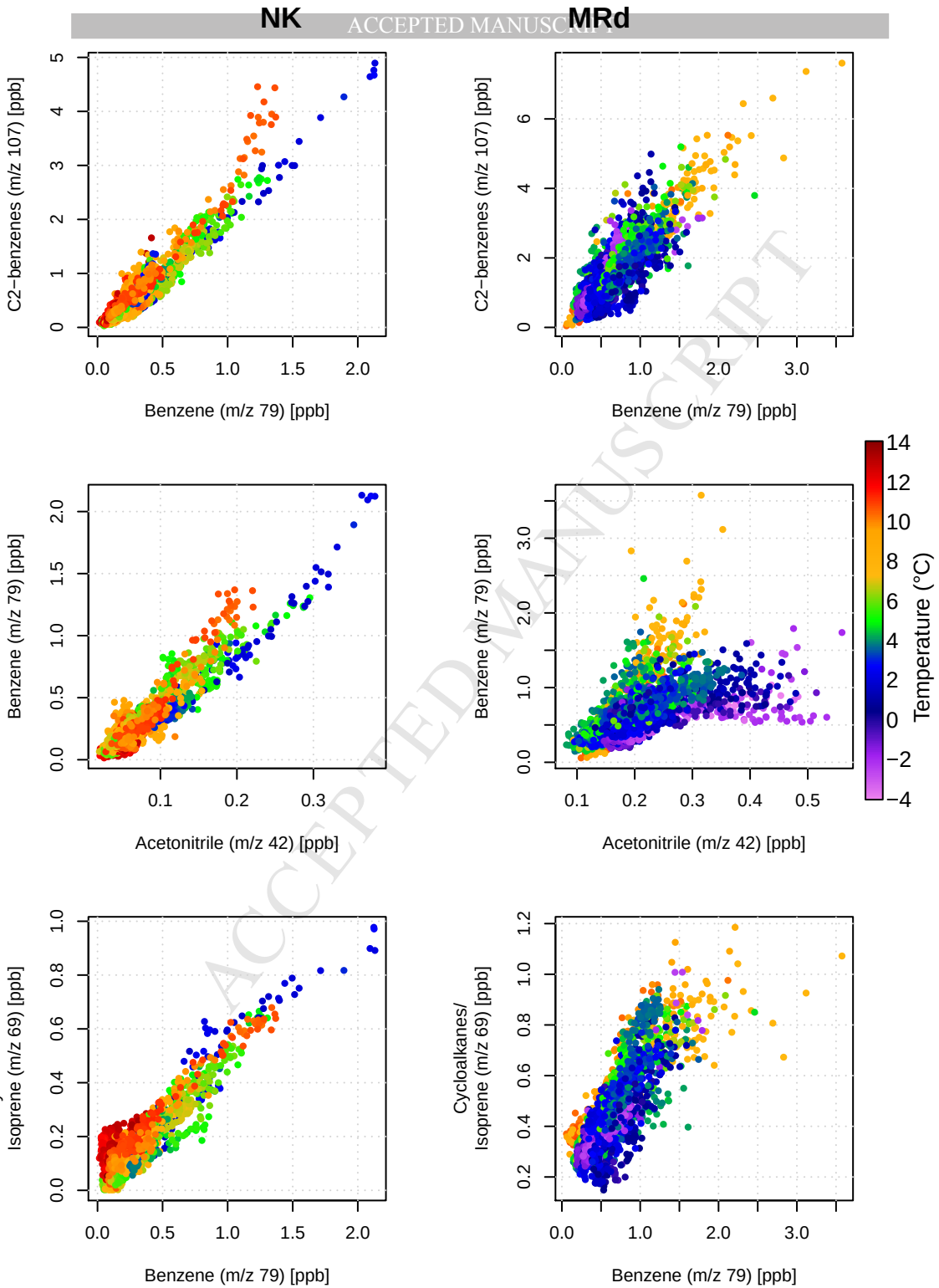
Frequency of counts by wind direction (%)











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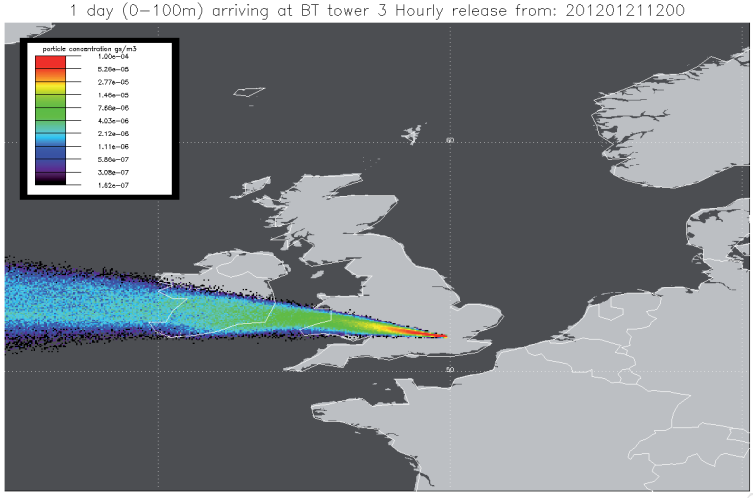

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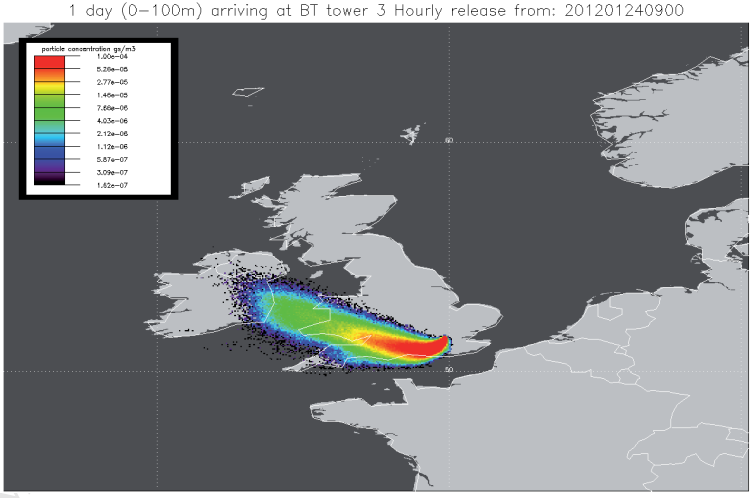

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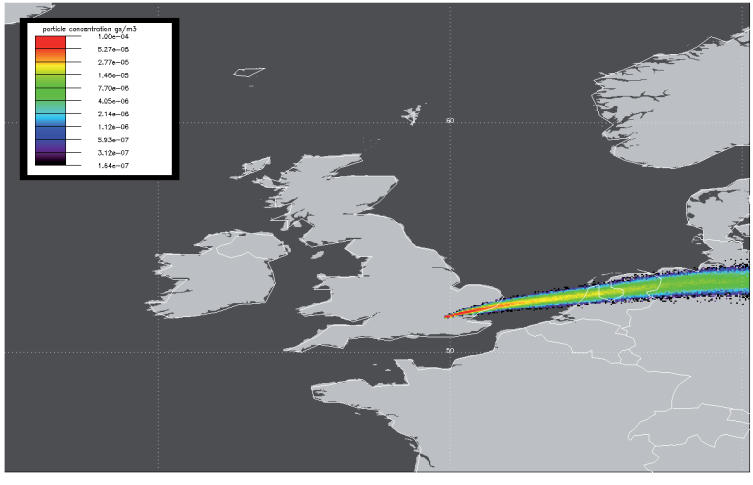

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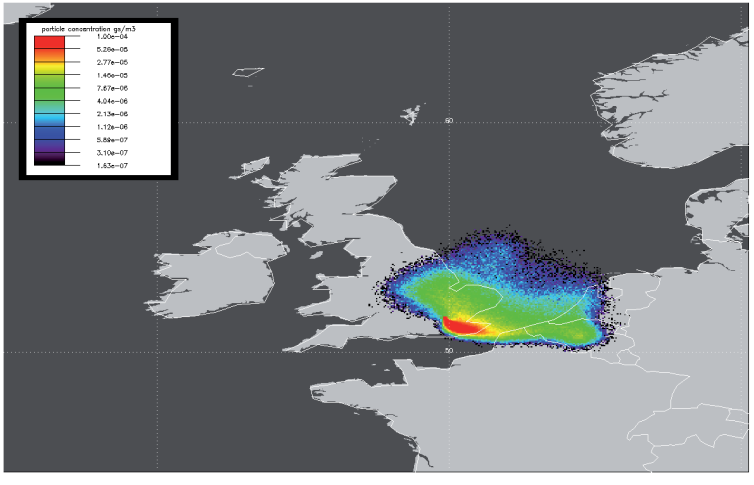
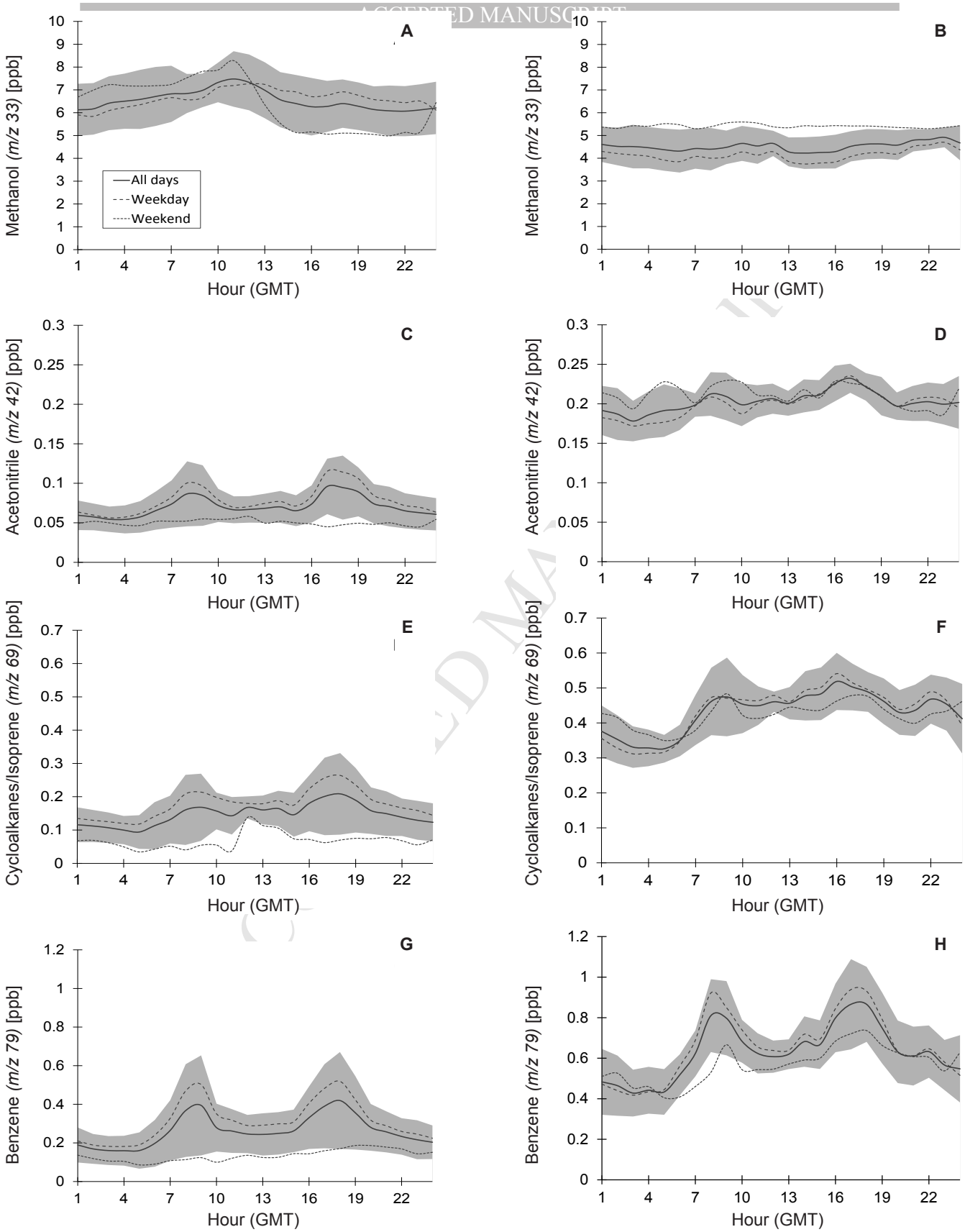
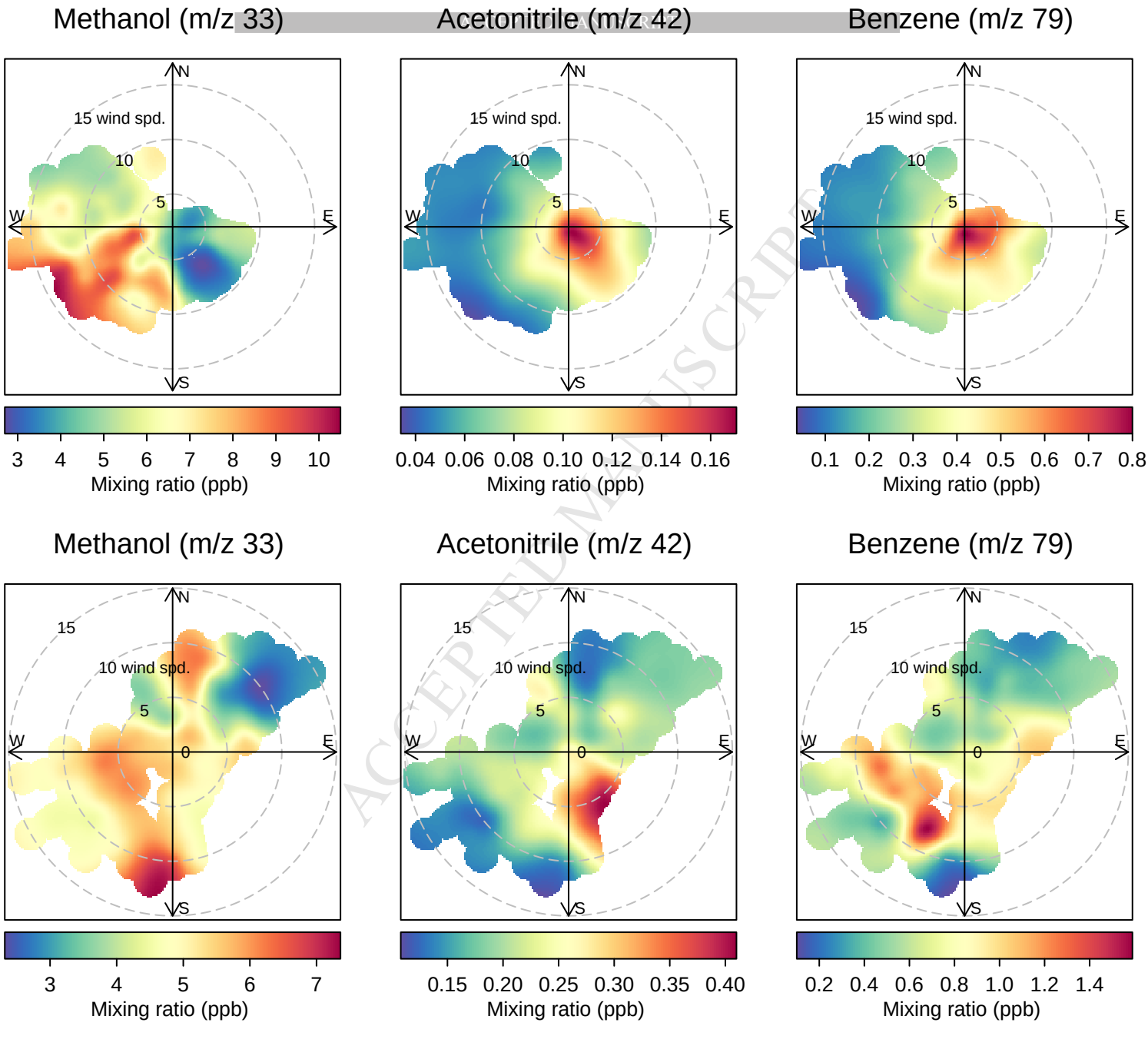


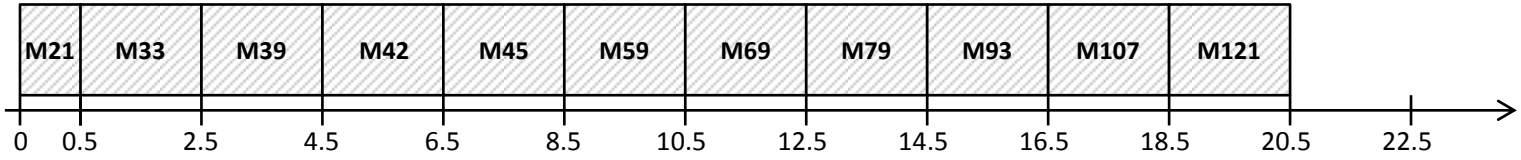




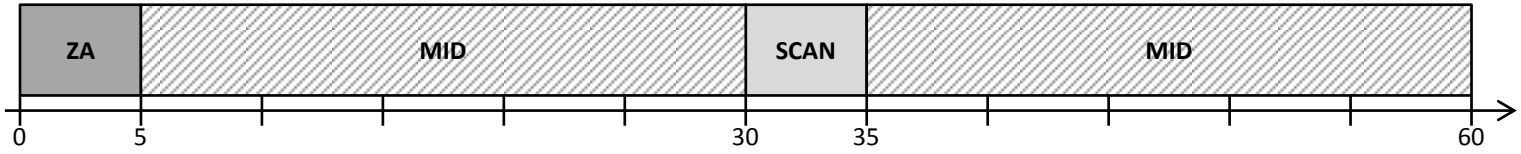
Highlights

- Volatile organic compound concentrations were measured in central London.
- Measurements were compared with the automatic hydrocarbon network.
- Vehicle emissions were the main source at both urban background and kerbside sites.
- Some effects of temperature on compound correlations were observed.
- Excellent qualitative agreement was seen between the measurement instruments.

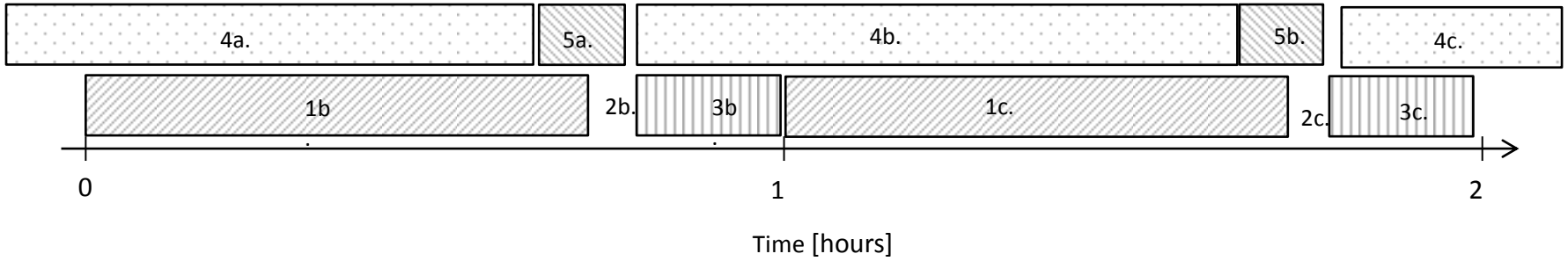
PTR-MS: MID measurement cycle

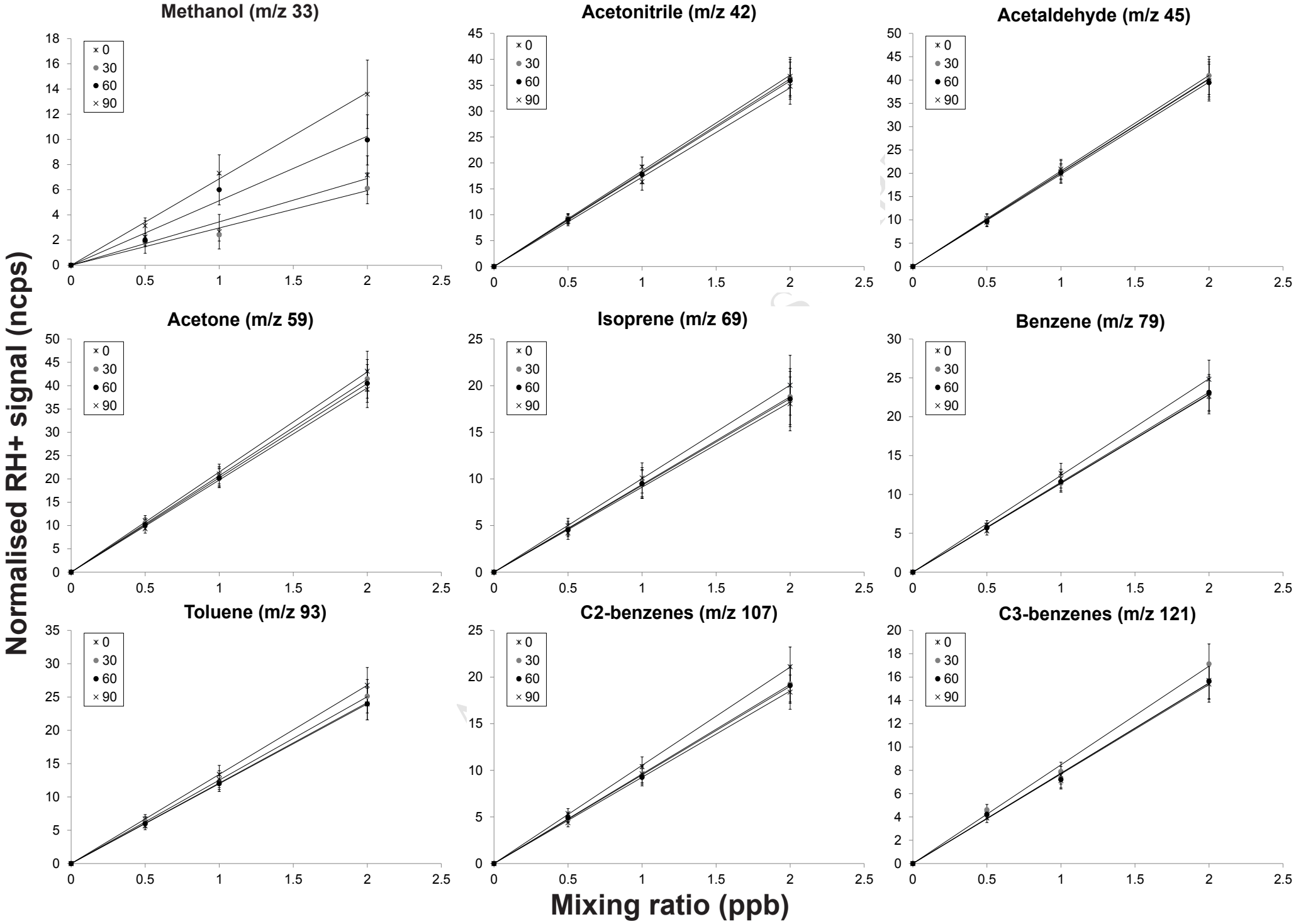


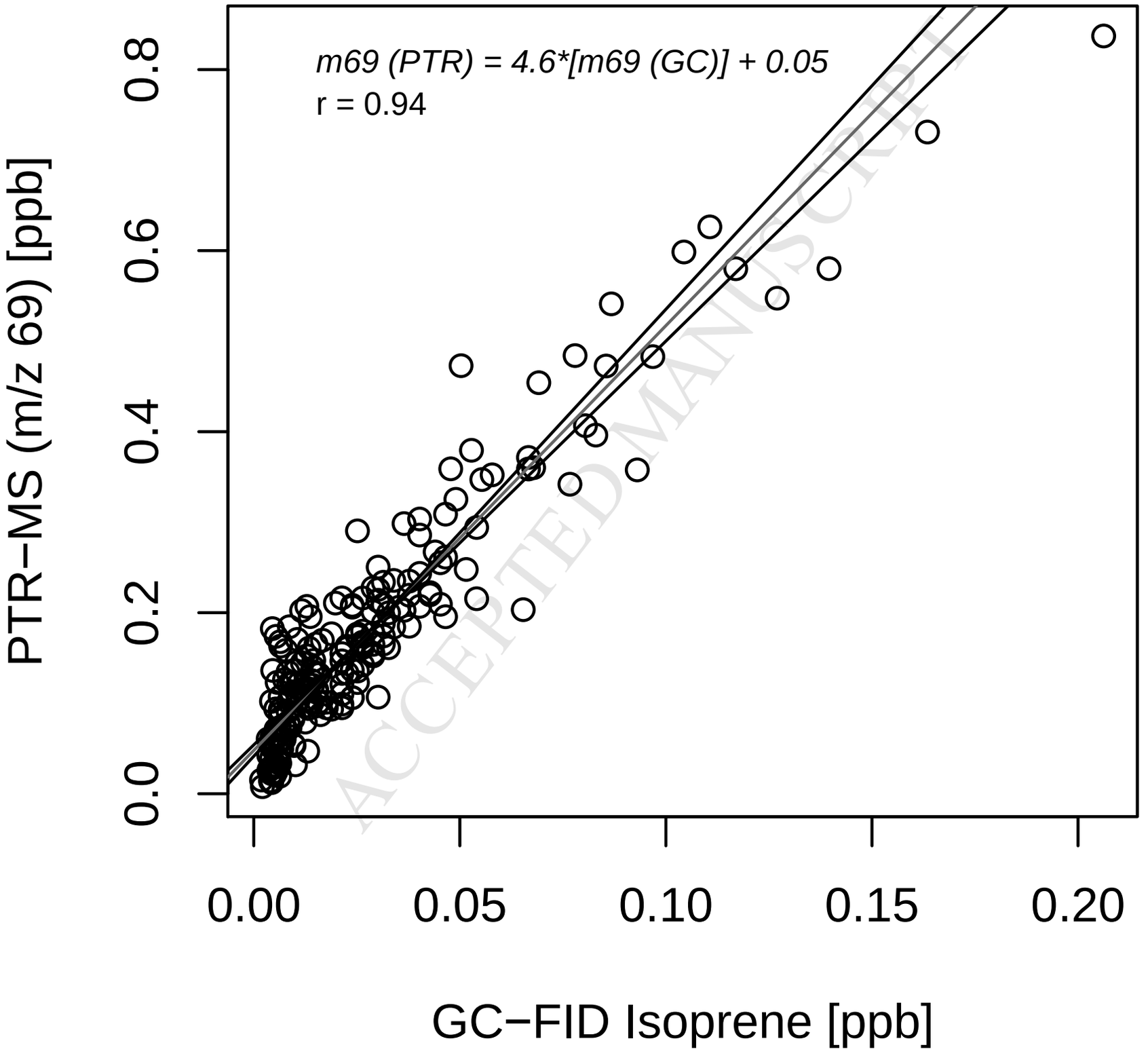
PTR-MS: 1h operating cycle



GC-FID operating cycle







Supplementary content

A. Details on measurement sites, instrument parameters and duty cycles for both PTR-MS and GC-FID

Extensive comparisons of the measurement sites and the mean meteorological measurements during the two measurement periods are summarised in Table A1.

A1. PTR-MS

A high-sensitivity proton transfer reaction- mass spectrometer (PTR-MS) fitted with three Varian turbo-molecular pumps and a 9.5 cm long drift tube was used for online measurements VOC mixing ratios. During each deployment of the PTR-MS, drift tube pressure, temperature and voltage were kept constant at 2.06 mbar, 48 ℃ and 550 V respectively to maintain an *E*/*N* ratio of 125 Td. Air was subsampled from the main line with an inlet flow rate of 0.25-0.3 l min^{-1}. The primary ion count (*m/z* 19) ranged between 6 - 14 x 10^6 cps with a mean of 11 x 10^6 cps. The $H_3O^+.H_2O^+$ water cluster ions ranged between 6.5 x 10^4 – 2.6 x 10^5 cps with a mean of 1.4 x 10^5 cps which represented on average 1.7% of the primary ion signal, while the O_2+ signal (*m/z* 32) was <2% of the primary ion signal. The 1 h measurement protocol consisted of 5 min zero air measurements using a zero air generator (Parker Balston, UK), then 25 min MID mode, followed by 5 min mass scans and another 25 min in MID mode (Figure A1). During the MID mode, 11 selected masses were measured with a dwell time of 2 s per mass and 0.5 s for the primary ion, resulting in a 20.5 s cycle time, whereas SCAN modes cycled through the mass range *m/z* 21 – 206 with a dwell time of 0.5 s each.

A2. GC-FID

The GC-FID method used by the AHN has recently been linked to the QA/QC procedures of the EU Infrastructure Project ACTRIS (www.actris.net). The method includes a TurboMatrix thermal desorption (TD) unit with an online sampling accessory to gather samples directly from ambient air. The TD extracts the compounds onto an adsorbent trap, which is cooled to -30℃. The analytes are then thermally desorbed and transported through a heated transfer line by a carrier gas to the GC. The GC contains two columns and compounds are separated by volatility into two fractions. The flame ionization detector (FID) monitors the chromatography on two columns. After a 40 min sampling period the sample is injected into the GC and the trap automatically begins collecting the next sample after 20 min ensuring hourly sample acquisition.

Inter-comparisons with the VOC standards used by the AHN were not possible, therefore uncertainties associated with the AHN standards cannot be discounted and may have

contributed to the offsets between the two methods. Especially in areas of high pollution, datasets from automated monitoring systems using GC-FID can also be susceptible to high variability, as was shown in Fortin et al., 2005, which would introduce additional uncertainty.

The GC-FID data were converted to ppbv using ambient pressure and temperature measurements which may also have introduced some uncertainty in the AHN data.

B. Calibrations and instrument background determination of the PTR-MS

The multi-component VOC gas standard (Ionimed Analytik GmbH, Austria, 1ppm +/- 5% uncertainty for all compounds) contained all VOCs selected for quantification by PTR-MS except *m/z* 121. After the campaign it was independently validated against another multi-component VOC standard (Apel Riemer Environmental Inc., CO, USA) containing the same compounds with the addition of a 1,2,4-trimethylbenzene. Uncertainties for all compounds were quantified in the Ionimed standard to be <10%, apart from methanol which was 15%.

The standard was diluted with air from the zero air generator. Normalized sensitivities were between 1.4 (*m/z* 121) and 11.9 (*m/z* 45) ncps $ppbv^{-1}$. The original instrument used for the measurements had been substantially upgraded, therefore a very similar instrument with similar specifications and performance indicators was used to investigate relative changes in background and sensitivity against humidity. These were thoroughly investigated in the laboratory using a range of relative humidites and all variations in sensitivity were within the overall calibration uncertainty (20% for methanol and <15% for all other compounds, see Figure B1). Sensitivities were comparable between instruments, although those of the original instrument started to decrease towards the higher masses. However, overall sensitivities correlated well ($r = 0.94$, $p < 0.001$) and since the same instrument parameters and conditions as during the campaign were maintained, it is assumed that instrument responses are comparable.

PTR-MS sensitivities of benzene and toluene in particular have been shown to depend on changes in relative humidity, i.e. when the fraction of $H_3O^+ \bullet (H_2O)$ ions in the reactor change (Warneke et al., 2001). For these two compounds the reaction with $H_3O^+ \bullet (H_2O)$ ions is energetically not permitted and does not occur (Spaněl and Smith, 2000). However, PTR-MS sensitivities have a less pronounced humidity dependency at higher *E/N* ratios because the reagent ions are dominated by H_3O^+ (de Gouw and Warneke, 2007). Although the absence of the reaction with *m/z* 37 for these two compounds was taken into account when normalising the signals, some humidity effects on background counts may have contributed to the offset, as humidity effects were determined post-calibration and had to be extrapolated resulting in large uncertainties.

A custom built zero air generator consisting of a platinum catalyst and charcoal heated to 200 ℃ was used to determine instrument background values. During the campaign dry air was used, however this was insufficient in accounting for variations due to humidity. Therefore, humidity effects were determined by humidifying the zero air over a range of relative humidities in the laboratory after the campaign. The instrument background for the campaign average relative humidity (72% with IQR 64-83%) was subtracted for compounds showing moderate humidity dependency. For compounds with stronger humidity effects a running correction based on the *m/z* 37/ *m/z* 19 ion ratio, which is a proxy for humidity, was applied. These corrections produced a minimal difference due to the low variability of *m/z* 37 counts during the campaign (0.8-2.6% with a mean of 1.7% of primary ion signal). Impurities in the inlet system during the campaign may have caused additional humidity dependency for aromatic species. These could not be accurately recreated when investigating humidity effects in the laboratory, hence this may have resulted in the remaining background offset for *m/z* 79, 93, 107 and 121. The largest offset was seen in *m/z* 121, which may be due to a number of factors (discussed in section 3.2 in more detail) including the fact that the instrument was only calibrated against one trimethyl benzene, as standards for many of the other contributing compounds were unavailable to calibrate separately. Correlations of the compound against relative humidity showed low coefficients (r between 0.08 and 0.3, $p>0.05$), which suggests most humidity effects were sufficiently accounted for, although a large uncertainty associated with the quantitative measurements remains, especially for the higher *m/z*.

Isobaric interferences from O_2+ ion on *m/z* 33 due to the $^{16}O^{17}O$+ isotope were accounted for, as this reacts with the water cluster in the drift tube causing a decrease in the instrument background signal with higher humidities. During the campaign, however, the O_2+ counts were always <2% of the primary ion count. Additionally, interference of a CCl_4 isotope at *m/z* 121 was subtracted. Since the Montreal Protocol the addition of this compound in fire extinguishers, cleaning agents, and precursors for refrigerants is prohibited and it is uniformly distributed throughout the atmosphere at around 0.1 ppb. This provides a constant contribution to *m/z* 121 in PTR-MS which can be subtracted.

C. Comparison of *m/z* 69 with isoprene concentrations measured by GC-FID

Globally isoprene is the dominant component of *m/z* 69, however due to the season and the urban location, the biogenic contribution was absent. Comparison of the PTR-MS data for *m/z* 69 against isoprene concentration measurements from a GC-FID at NK (courtesy of J. Hopkins and R. Holmes) showed that the isoprene signal of *m/z* 69 was around 22% after correcting for the instrument background signal (Figure C1). However, correlations with the

isoprene concentrations were high ($r = 0.94$, $p<0.001$). The remaining offset could be from isobaric interference from other compounds such as cyclic alkanes, which share emission sources with anthropogenic isoprene, in which case they represent a considerable contribution to *m/z* 69 (Yuan et al., 2014). Alternatively, it may be possible that, as seen in the aromatic compounds, the large uncertainties associated with the calibration (15% total uncertainty) or the background corrections of the PTR-MS resulted in the offset.

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133 **Table A1. Summary of site descriptions for measurements sites at North Kensington and Marylebone Rd,**
134 **London and campaign average meteorology.**

	North Kensington	Marylebone Road
Time period	16 - 25 January 2012	25 January - 7 February 2012
Site category [a]	Urban background (class A)	Urban kerbside (class A)
Area	Sion Manning School courtyard	Automatic Hydrocarbon Network[c] cabin
Coordinates (altitude)	51°31'15.18"N; 0°12'48.85"W (25m.s.l.)	51°31'21.14"N; 0°09'16.59"W (35m.s.l.)
Surroundings	Residential, <10m buildings to N and W, main road 95m E and A40 Westway 500m S (70 000- 100 000 vehicles per day)	Commercial, A501 Marylebone Rd (70 000 vehicles per day) 1.5m N, intersection Luxborough Street, Regent's Park (green area of 166 ha) 200 m N
Oke 2006 (UCZ[b]) category	3	2
Inlet height (m)	4.7	2.5
Tube length (m)	7	4
Mean temperature (°C)	7.8 ±2.9[d1]	3.0 ±2.8[d2]
Mean RH (%)	71.8 ±12.2 [d1]	68.4 ±12.0 [d2]
Precipitation (mm)	3 [d1]	11 [d2]
Mean wind speed (m s^{-1})	1 (at 4.7m) [d1]	6.4 (at 191m) [d2]
Mean wind direction (°)	205 (SSW) [d1]	62 (ENE) [d2]

135 [a]Site classification: Category A indicates sites highly representative of emissions for intended areas.
136 [b] Urban Climate Zone classifications by Oke, 2006.
137 [c] Permanent measurement site run by the Department for Environment, Food and Rural Affairs (DEFRA)
138 [d1] Data from WXT520 weather sensor (Vaisala Ltd, Finland) at NK
139 [d2] Data from WXT520 weather sensor at BT tower near MRd
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Figure captions

Figure A1. Top) Representation of the PTR-MS measurement cycle used at both North Kensington and Marylebone Rd sites. The multiple ion detection (MID) cycle lasted 20.5 sec and was repeated during 25 min. **Bottom)** Approximation of the measurement cycle used by the Automatic Hydrocarbon Network GC-FID at the Marylebone Rd measurement site. Multiple sample analyses are indicated by *a* (previous hour), *b* (hour 1.) and *c* (hour 2.). Each cycle consists of the following stages: 1. Sample acquisition (40 min), 2. analytes are injected into GC columns, 3. trap cooling in preparation for the next sample acquisition (15 min), 4. GC analysis (50 min), and 5. GC cooling in preparation for the next sample analysis (Yardley et al., 2012).

Figure B1. Post-campaign calibrations over a range of relative humidities (0, 30, 60, 90% +/- 5%) for all nine selected compounds (methanol [*m/z* 33], acetonitrile [*m/z* 42], acetaldehyde [*m/z* 45], acetone [*m/z* 59], isoprene [*m/z* 69], benzene [*m/z* 79], toluene [*m/z* 93], o-xylene [*m/z* 107], and 1,2,4-trimethylbenzene [*m/z* 121]) .

Figure C1. Comparison of 1 h averages of *m/z* 69 (ppb) measured by PTR-MS against isoprene concentrations measured by GC-FID (ppb) at North Kensington during 16th – 25th Jan 2012 showing the linear regression with correlation coefficient (r). We gratefully acknowledge James Hopkins and Rachel Holmes (University of York) for making the data available for analysis.